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On the Preparation of the Aryl Isothiocyanates.

BY F. B. DAINS, R. Q. BREWSTER, C. P. OLANDER.

THE aromatic mustard oils, RNCS, which have been the subject of many investigations on account of their reactivity, have been prepared by a number of different methods. The most common one involves the synthesis of the disubstituted thioureas from the amines and the subsequent splitting of the thioureas into aryl isothiocyanates and the amine or some derivative. Thus thiocarbanilide, when boiled with concentrated hydrochloric acid, 20 per cent sulphuric acid or concentrated phosphoric acid gave phenyl mustard oil and varying amounts of aniline and triphenyl guanidine.

The yield of mustard oil, based on the aniline used, in general is far from satisfactory on account of losses incurred in the preparation of the thiourea and the subsequent splitting with acid.[1]

An interesting modification in the preparation of these compounds depends upon the action of acetic anhydride or an acid chloride such as acetyl chloride upon the thiourea.[2] The acetyl derivative of the thiourea, which is first formed, readily breaks down into the mustard oil and an acyl-aryl amide,

$$RNHCSNCOCH_3R = RNCS + RNHCOCH_3.$$

While the above methods are of general applicability, it is evident that only one-half of the original amine can be converted into the isothiocyanate, and that it necessitates the synthesis of the substituted thiourea.

Fortunately, however, H. S. Fry's[3] interesting method for the preparation of the diaryl thiocarbamides has made readily accessible various thioureas that were difficult to obtain by the older methods.

1. J. 1858, 394. Z. 1869, 359. Ber. 15, 986 (1882).
2. J. Chem. Soc., 59, 400 (1891). J. Am. Chem. Soc., 22, 188 (1900).
3. J. A. Chem. Soc., 35, 1539 (1903).

A second general method for the synthesis of the mustard oils is based upon the intermediate formation of the salt of a substituted dithiocarbamic acid, RNHCSSMe. This is illustrated by the Hofmann[4] syntheses of alkyl isothiocyanates, which involve the desulphurization of the salt $RNHCSSNH_3R$ with mercuric chloride, silver nitrate, etc.

In the aromatic series compounds of the type $RNHCSSNH_3R$ cannot, as a rule, be isolated, but instead lose hydrogen sulphide and go over to the ordinary thiourea, RNHCSNHR. On the other hand, the aryl amines react with carbon bisulphide and ammonia and give almost quantitatively the corresponding ammonium salts, $RNHCSSNH_4$. This should afford a convenient source of mustard oils, provided some simple means could be devised for removing a mole of NH_4SH.

METHODS FOR SUCH ELIMINATION.

Andreasch[5] and others have shown that the ammonium dithiocarbamates react with ethyl chloroformate with the formation of aryl isothiocyanates, RNCS. The yields, however, are varying and the products are apt to be contaminated with the corresponding oxygen ureas. The method involves, too, the use of the expensive ethyl chloroformate.

In a paper published in 1891, Losanitsch[6] described a number of salts of phenyl dithiocarbamic acid and obtained from the ammonium dithiocarbamate, in water solution, the corresponding colored salts of copper, nickel, cobalt, iron, mercury and manganese. The statement was made "that the best method for the preparation of phenyl mustard oil is to treat a solution of ammonium phenyl dithiocarbamate with copper sulphate and distill with steam. The yield of mustard oil is theoretical." No confirmatory data, however, were given for this statement. Later Heller and Bauer[7] found that lead carbonate reacted with the ammonium aryl dithiocarbamates, yielding mixtures of the aryl isothiocyanates and monoaryl thioureas.

Since considerable amounts of the aryl isothiocyanates were needed in another investigation in this laboratory, it seemed advisable to follow up this observation of Losanitsch and ascertain

4. Ber. 1, 170 (1868). Ber. 8, 108 (1875). Ann. 371, 201 (1909).
5. Monat. 27, 1211 (1906). Monat. 30, 701 (1909). Monat. 33, 363 (1912). Am. Ch. J. 24, 432 (1902). Ber. 35, 3368 (1902). Ber. 36, 3520 (1903). Ber. 40, 2198 (1912).
6. Ber. 24, 3021 (1891).
7. J. Prak. Ch. (2) 65, 365 (1902).

whether the method was really a practical one and to determine if possible the optimum conditions.

The investigation has shown that the general method suggested by Losanitsch is capable of giving very satisfactory results in the synthesis of aryl isothiocyanates. Yields of mustard oil up to 77 per cent based upon the weight of the amine have been obtained—a result which is impossible by the usual method.

REACTIONS INVOLVED IN THE DESULPHURIZATION OF THE ARYL DITHIOCARBAMATES.

Using aniline as a typical aryl amine the synthesis is best illustrated by the following reactions:

I. $C_6H_5NH_2 + CS_2 + NH_4OH = C_6H_5NHCSSNH_4 + H_2O.$

II. $C_6H_5NHCSSNH_4 + Pb(NO_3)_2 = C_6H_5NCS + NH_4NO_3 + HNO_3 + PbS.$

Equation II does not occur directly, since the addition of the lead nitrate causes the precipitation of the lead salt—

III. $2C_6H_5NHCSSNH_4 + Pb(NO_3)_2 = (C_6H_5NHCSS)_2Pb + 2NH_4NO_3.$

The lead phenyl dithiocarbamate on heating breaks down as follows:

IV. $(C_6H_5NHCSS)_2Pb = C_6H_5NCS + C_6H_5NHCSSH + PbS.$

The free phenyl dithiocarbamic acid tends to decompose with the formation of thiocarbanilide, aniline, etc. To prevent this a second mole of lead nitrate is used:

V. $(C_6H_5NHCSS)_2Pb + Pb(NO_3)_2 = 2C_6H_5NCS + 2PbS + 2HNO_3.$

Since the nitric acid diminishes the yield by freeing phenyl dithiocarbamic acid from its NH_4 salt, an excess of ammonium hydroxide is added. The ideal proportions would be:

VI. $2C_6H_5NHCSSNH_4 + 2Pb(NO_3)_2 + 2NH_4OH = 2C_6H_5NCS + 2PbS + 4NH_4NO_3.$

For the best results, the solution after the addition of the lead nitrate should be neutral or only slightly acid. An excess of ammonia converts the mustard oil into monophenyl thiourea.

EXPERIMENTAL.

PREPARATION AND ISOLATION OF THE AMMONIUM PHENYL DITHIOCARBAMATE.

The following procedure, which is a modification of the method described by Heller and Bauer,[8] was found to give the best results. Carbon bisulphide (54 gms.) and 28 per cent ammonium hydroxide

8. J. Prak. Chem. (2) 65, 369 (1902).

(80 gms.) were mixed in a wide-mouthed flask or tall beaker set in ice. To this was added through a dropping funnel, in the course of 15 minutes, aniline (54 gms.), the whole being kept in agitation with an automatic stirrer.

The milky heterogeneous mixture, which first resulted, became clear and homogeneous after the addition of the aniline. The ammonium salt soon began to separate, and the mixture may become so thick as to stop the stirrer. After standing an hour in the ice bath the white ammonium salt was filtered, the mass washed with a little alcohol and dried quickly on a porous plate or between filter paper. The best yield of this salt was 86 per cent of the theory, although this may vary decidedly, not only in the case of aniline but also with the other aryl amines. This is due to the incomplete separation of the ammonium salt rather than to its nonformation.

PROPERTIES OF THE AMMONIUM PHENYL DITHIOCARBAMATE.

On standing, the salt slowly decomposed with the formation of hydrogen sulphide, ammonia, carbon bisulphide, aniline and thiocarbanilide. The decomposition was hastened when the salt was boiled with water. The results here indicated that the two main reactions were as follows, the first predominating:

I. $C_6H_5NHCSSNH_4 = C_6H_5NH_2 + CS_2 + NH_3$.
II. $C_6H_5NHCSSNH_4 = C_6H_5NCS + H_2S + NH_3$.

The mustard oil and aniline reacted to give thiocarbanilide, but the yield is low, only about 20 per cent of the theoretical.

With the ammonium salts of the p-chloro and p-bromophenyl dithiocarbamates, where the amines and isothiocyanates are less volatile, 55 to 60 per cent yields of the substituted thiocarbanilides have been obtained by this method.

DECOMPOSITION WITH ACIDS.

When an aqueous solution of the salt is treated with hydrochloric acid the quantitative decomposition can be expressed as follows:

$$C_6H_5NHCSSNH_4 + 2HCl = C_6H_5NH_2HCl + CS_2 + NH_4Cl.$$

Only traces of hydrogen sulphide and phenyl isothiocyanate are formed.

PREPARATION OF THE ARYL ISOTHIOCYANATES FROM THE AMMONIUM SALTS.

It is evident, then, that in order to produce the mustard oil, RNCS, from the dithiocarbamate, $RNHCSSNH_4$, some metallic salt must be used which will form a stable sulphide and an ammonium

salt. To determine the best conditions for such a decomposition the following experiments were undertaken, using the dry ammonium salt of the aryl dithiocarbamates.

FERROUS SULPHATE.

A solution of 60 gms. of the iron salt in the minimum volume of water was added to 40 gms. of the ammonium phenyl dithiocarbamate in 200 cc. of water. A yellowish-brown precipitate formed immediately. The mixture, which had a noticeable odor of the phenyl isothiocyanate, was allowed to stand for an hour and then distilled with steam, but with the result that only 3 cc. of an impure mustard oil was obtained.

ZINC SULPHATE.

On mixing 30 gms. of the ammonium salt in 300 cc. of water with 47 gms. of zinc sulphate in 150 cc. of water a thick, white precipitate of the zinc phenyl dithiocarbamate was formed. This changed on steam distillation to zinc sulphide and gave a 23 per cent yield of the phenyl isothiocyanate.

COPPER SULPHATE.

To a solution of 25 gms. of the ammonium salt in 150 cc. of water was added 34 gms. of copper sulphate in the same volume of water. The odor of mustard oil was very pronounced, and the yellowish-brown copper salt changed readily, on distilling the mixture with steam, to the black copper sulphide. The yield of oil in this case was 71.7 per cent—a very decided increase.

LEAD NITRATE.

Using the same concentrations as above, 25 gms. of the ammonium salt and 40 gms. of lead nitrate gave the brown lead salt with a subsequent yield of 77.2 per cent phenyl isothiocyanate—a maximum which has not been exceeded.

In general it has been found that while both the copper and lead salts are suitable desulphurizing agents, the use of lead nitrate gave the better result in about the above ratio.

PREPARATION OF PHENYL ISOTHIOCYANATE WITHOUT SEPARATION OF THE AMMONIUM SALT.

The data obtained from the preparation of the ammonium salts of the aryl dithiocarbamates showed that the isolation of this compound might be far from quantitative, with the result that the yield of mustard oil based on the amine used would be proportionately lowered. This was proved directly by many experiments, two of which will be described in detail.

In each case the following amounts of reagents were used and the same procedure followed as exactly as possible:

Aniline	26 gms.
Carbon bisulphide	27 gms.
Ammonium hydroxide (28%)	44 gms.
Alcohol	20 cc.
Lead nitrate	100 gms.

The addition of the aniline required one-half hour. The stirring was then continued for another one-half hour, and the mixture filtered after standing for an additional hour. The separated salt was dissolved in 200 cc. of water, treated with the lead nitrate (in 200 cc. water), and distilled with steam. The yield of pure mustard oil was 20 gms. (53 per cent).

In the second case the unfiltered solution and salt was made up to 200 cc. with water and desulphurized as before. The product weighed 28 gms.—a yield of 74.2 per cent, based on the aniline used. The best yield obtained under these conditions was 76.8 per cent pure phenyl isothiocyanate. The difference in yield in the above experiments between 53 per cent and 74 per cent is due without question to the solubility of the ammonium salt in the aqueous ammonia.

LABORATORY PREPARATION.

The following directions are given as suitable for a laboratory experiment in the preparation of the phenyl isothiocyanate:

Place 54 grams of carbon bisulphide and 80 grams of conc. NH_4OH (28 per cent) in a tall beaker, surrounded by ice, and stir the mixture with a turbine. Drop 56 gms. of aniline into this mixture from a separatory funnel during the course of 20 minutes. The separation of ammonium phenyl dithiocarbamate soon begins. Continue the stirring for 30 minutes after all of the aniline has been added. Then allow the mixture to stand for another period of 30 minutes without stirring.

Dissolve the salt by the addition of 800 cc. of water, and add to the solution (with constant stirring) 200 gms. of lead nitrate dissolved in 400 cc. of water. Steam-distill the product from a 5-liter flask.

Put in the receiver a little dilute sulphuric acid; this will combine with traces of ammonia or aniline that might be driven over, and thus prevent the formation of any mono- or diphenyl thiourea.

LARGER-SCALE PRODUCTION.

The preparation of the mustard oil was carried out in a number of experiments, using from five to ten times the amount of the reagents listed above, with corresponding dilution. The percentage yields, however, were not so great as with smaller amounts. For instance, 280 gms. of aniline gave 232 gms. of product, and 560 gms. of aniline yielded 435 gms. of pure redistilled phenyl isothiocyanate. The low results were due in part to difficulties in properly mixing the reagents. If much free nitric acid was formed it decomposed the ammonium phenyl dithiocarbamate, thus preventing the formation of the lead phenyl dithiocarbamate. Other by-products that occurred were ammonium thiocyanate, diphenyl thiourea, triphenyl guanidine, which appeared as the nitrate, and monophenyl thiourea, where any excess of ammonia was present. In addition a strong current of steam is needed to separate the oil from the mass of lead sulphide formed.

ACTION OF LEAD NITRATE ON OTHER SALTS OF THE PHENYL DITHIOCARBAMIC ACID.

It seemed worth while to try the desulphurization of other than the ammonium salts, since in the absence of that reagent certain side reactions might be prevented.

Sodium Salt. $C_6H_5NHCSSNa$.

Aniline	28.0 gms.
Carbon bisulphide	27.0 gms.
Sodium hydroxide	13.1 in 50 cc. water.
Lead nitrate	100.0 in 300 cc. water.

The sodium salt which formed on mixing the reagents was so thick that the stirrer was stopped. Alcohol, 22 cc., was therefore added, and the stirring continued for one-half hour. After standing for an hour the orange-colored mixture was dissolved in 300 cc. of water and treated with the lead nitrate solution. Only a 30.2 per cent yield of the mustard oil was obtained, the greater portion of the aniline having been converted into thiocarbanilide.

Barium Salt. $(C_6H_5NHCSS)_2Ba$.

Aniline	28 gms.
Carbon bisulphide	30 gms.
Crys. barium hydroxide	47.5 gms. in 110 cc. of water.
Zinc chloride	42.1 gms. in 42 cc. of water.
Sodium hydroxide	9.6 gms. in 18 cc. of water.

The aniline was slowly added to the mixture of barium hydroxide

and carbon bisulphide and then stirred for an additional hour. The odor of hydrogen sulphide became noticeable, showing decomposition. The zinc hydroxide formed by the addition of the sodium hydroxide to the zinc chloride was now added and the mixture allowed to stand overnight. On distillation with steam, 15.2 gms. of mustard oil, or 37.4 per cent, was isolated.

CALCIUM SALT. $(C_6H_5NHCSS)_2Ca$.

Parallel experiments were now made, substituting calcium for barium hydroxide, the other conditions remaining the same. Very little phenyl isothiocyanate was obtained, the main product being thiocarbanilide.

In the report on "The Manufacture of War Gases in Germany,"[9] it is stated that Kalle & Co. made the phenyl mustard oil used in the preparation of phenyl iminophosgene from the calcium phenyl dithiocarbamate, which was then desulphurized with a mixture of zinc chloride and sodium hydroxide.

That calcium phenyl dithiocarbamate was formed from the carbon bisulphide and calcium hydroxide was shown in the following experiment:

Aniline	28.0 gms.
Carbon bisulphide	27.2 gms.
Calcium hydroxide	12.0 gms. in 26 cc. of water.
Lead nitrate	100.0 gms. in 300 cc. of water.

On the addition of the aniline there was a tendency for the mass to collect in a gummy paste. This was prevented by the addition of a little alcohol and stirring the mixture for 24 hours. After desulphurization with lead nitrate 15.6 gms. of oil were isolated, which corresponded to a yield of 38.4 per cent. The increase in mustard oil is doubtless due to longer stirring and the more efficient desulphurizing agent, lead nitrate.

PREPARATION OF OTHER ARYL ISOTHIOCYANATES.

The following experiments were carried out in order to ascertain whether the method was suitable for the preparation of other aryl isothiocyanates:

o-TOLYL ISOTHIOCYANATE. $o\text{-}C_7H_7NCS$.

o-Toluidine	32.2 gms.
Carbon bisulphide	27.0 gms.
Ammonia water	47.0 gms.
Alcohol	20.0 cc.
Lead nitrate	100.0 gms. in 200 cc. water.

9. J. F. Norris, J. Ind. Eng. Chem. 11, 827 (1919).

The ammonium salt crystallized out readily after addition of the amine. The mixture was then brought into solution by the addition of 400 cc. of water and treated as before. The weight of pure o-tolyl mustard oil was 32.8 gms., or 73.27 per cent.

m-Tolyl Isothiocyanate. m-C_7H_7NCS.

Using the same proportions as before, the solid ammonium salt, which is easily soluble in water, soon formed. From the reaction mixture was isolated 33.5 gms. of oil, or 74.7 per cent yield.

p-Tolyl Isothiocyanate. p-C_7H_7NCS.

Under the above conditions 32.3 gms. (72.1 per cent) of the p-tolyl mustard oil (b. p. 270) were obtained.

1, 3, 4,-Xylyl Isothiocyanate. $(CH_3)_2C_6H_3NCS$.

1, 3, 4-Xylidine	36.4 gms.
Carbon bisulphide	27.0 gms.
Ammonium hydroxide	47.0 gms.
Lead nitrate	100.0 gms. in 200 cc. of water.

After three hours' stirring the ammonium salt separated in coarse crystals, which were dissolved in 400 cc. of water before the addition of the lead nitrate. The mustard oil was very slowly volatile with steam, and was obtained partly by this method and partly by extraction of the oily lead sulphide with carbon bisulphide. The separation was not complete, and only 25.5 gms. (52 per cent) of the xylyl isothiocyanate (m. p. 31°) were obtained.

Pseudocumyl Isothiocyanate. 1, 2, 4, 5, $(CH_3)_3C_6H_2NCS$.

Pseudocumidine	20.0 gms.
Carbon bisulphide	15.0 gms.
Ammonium hydroxide	23.0 gms.
Alcohol	22.0 cc.
Lead nitrate	49.0 gms.

The ammonium salt separated after two hours' stirring. It was dissolved in 1,000 cc. of water and treated with the lead nitrate in the same dilution. The isothiocyanate is difficultly volatile with steam, and the yield, 50.2 per cent, could probably have been increased by extracting the sulphide residue with some solvent.

Alpha-Naphthyl Isothiocyanate. A-$C_{10}H_7NCS$.

Alpha-naphthylamine	20.0 gms.
Carbon bisulphide	15.0 gms.
Ammonium hydroxide	22.0 gms.
Alcohol	20 cc.
Lead nitrate	46.2 gms. in 200 cc. of water.

The reaction mixture was dark colored and required long stirring before the ammonium salt separated. It was then dissolved in 400 cc. of water and desulphurized.

The isothiocyanate, which melted at 35°, was isolated by extracting the sulphide precipitate with repeated portions of alcohol. The product weighed 17.6 gms. (68.2 per cent).

BETA-NAPHTHYL ISOTHIOCYANATE.

The procedure was the same as with the alpha-naphthylamine, and while the ammonium salt, which was readily formed, reacted with the lead nitrate, no isothiocyanate could be isolated from the residue using alcohol as a solvent. It is probable that some other solvent would have proved more suitable.

o-ANISYL ISOTHIOCYANATE. o-$CH_3OC_6H_4NCS$.

o-Anisidin	37.1 gms.
Carbon bisulphide	27.0 gms.
Ammonium hydroxide	47.0 gms.
Alcohol	20 cc.
Lead nitrate	100.0 gms. in 200 cc. of water.

The ammonium salt separated quickly as a mass of coarse crystals. The mixture was allowed to stand for one hour and then dissolved in 800 cc. of water and desulphurized. The mustard oil, which distilled slowly with steam, weighed 35.2 gms. (70.7 per cent).

p-ANISYL ISOTHIOCYANATE. p-$CH_3OC_6H_4NCS$.

p-Anisidine	10.0 gms.
Carbon bisulphide	10.0 gms.
Ammonium hydroxide	13.0 gms.
Alcohol	15.0 cc.
Lead nitrate	27.0 gms. in 500 cc. of water.

The salt formed readily in large white crystals. After standing two hours the mixture was dissolved in 500 cc. of water and treated as usual. The mustard oil was easily volatile with steam and gave a yield of 9.2 gms. (68.6 per cent).

p-PHENETIDYL ISOTHIOCYANATE. p-$C_2H_5OC_6H_4NCS$.

In this case the weight of p-phenetidine was 41.3 gms.; otherwise the amounts of reagents corresponded to those used in the preparation of the o-anisyl isothiocyanate. The mustard oil distilled slowly with steam and gave a yield of 72.7 per cent.

HALOGEN SUBSTITUTED PHENYL MUSTARD OILS.

m-Bromophenyl Isothiocyanate. m-BrC_6H_4NCS.

m-Bromoaniline	15 gms.
Carbon bisulphide	10 gms.
Ammonium hydroxide	13.6 gms.
Lead nitrate	29.0 gms. in 500 cc. of water.

The dithiocarbamate formed very slowly and coarse crystals of the ammonium salt began to appear only after an hour's stirring. These were dissolved in 500 cc. of water.

The oil which came over with the steam solidified on cooling. The yield, however, was only 7 gms. (37.4 per cent).

p-Bromophenyl Isothiocyanate. p-BrC_6H_4NCS.

The same quantity of reagents were used as in the preceding preparation except that 15 cc. of alcohol was added in order to decrease the solubility of the ammonium salt, which separated in the form of fine, needle-shaped crystals. After standing overnight the mixture was dissolved in 500 cc. of water and filtered from a little unchanged p-bromoaniline. The yield of mustard oil was 39.6 per cent.

p-Chlorophenyl Isothiocyanate. p-ClC_6H_4NCS.

p-Chloroaniline	20.0 gms.
Carbon bisulphide	15.0 gms.
Ammonium hydroxide	24.5 gms.
Alcohol	20 cc.
Lead nitrate	52.0 gms.

The mixture containing the ammonium dithiocarbamate was dissolved in 500 cc. of water and treated as usual. The yield was 15.8 gms. of the solid isothiocyanate (59.6%).

p-Iodophenyl Isothiocyanate. p-IC_6H_4NCS.

p-Iodoaniline	20 gms.
Carbon bisulphide	12 gms.
Ammonium hydroxide	14.2 gms.
Alcohol	20 cc.
Lead nitrate	30.2 gms.

The crystals separated after 30 minutes' stirring. The mixture after standing for four hours was added to 500 cc. of water, and later filtered from a dark-colored insoluble residue. The mustard oil, which was obtained in a 53.4 per cent yield, was volatile with steam and melted at 79°.

p-Nitroaniline.

All efforts to prepare the ammonium p-nitrophenyl dithiocarbamate failed, the nitroaniline being recovered unchanged.

RÉSUMÉ OF RESULTS.

Aryl isothiocyanates.	Per cent yields based on amines used.
Phenyl	76.8
o-Tolyl	73.2
m-Tolyl	74.7
p-Tolyl	72.1
1, 3, 4,-Xylyl	52.0
Pseudocumyl	50.7
Alpha-naphthyl	68.0
Beta-naphthyl	00.0
o-Anisyl	70.7
p-Anisyl	68.6
p-Phenetidyl	72.7
m-Bromophenyl	37.4
p-Bromophenyl	39.6
p-Chlorophenyl	59.3
p-Iodophenyl	53.3
p-Nitrophenyl	00.0

From the consideration of the foregoing results, it is evident that the success of the method is dependent upon at least three factors: First, the completeness of the formation of the ammonium aryl dithiocarbamate, $RNHCSSNH_4$. Second, the ease and completeness of separation from the sulphide precipitate. Third, the avoidance of side reactions leading to the formation of free aryl dithiocarbamic acid, aniline, etc. The low yield in the case of the xylyl, cumyl and alpha-naphthyl derivatives would seem to be due to their slight volatility with steam and the difficulty of extracting the oils from the mass of lead sulphide.

The cause of the failure with beta-naphthylamine must be determined by further investigation.

With the halogen substituted anilines which are less basic than the aniline, toluidine, etc., there is probably incomplete salt formation, which would thus account for the lower yields.

SUMMARY.

The paper describes a method for the preparation of aryl isothiocyanates which is relatively simple and inexpensive and which gives yields greater than any which require the intermediate formation of the diaryl thioureas.

□